Multilayer relaxation of Cu(210) studied by layer-doubling LEED analysis and pseudopotential density functional theory calculations

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Multilayer relaxation of Cu(210) surface has been studied by layer-doubling low energy electron diffraction (LEED) analysis and pseudopotential density functional theory (DFT) calculations. An excellent agreement between the calculated and measured *I-V* curves has been achieved as judged by direct inspection and a small Pendry *R* factor of 0.12. We suggest that the layer-doubling method is a suitable choice for quantitative LEED structural studies on high-index metal surfaces with interlayer spacings down to 0.8 Å. Our pseudopotential DFT calculations have reproduced the relaxation sequence determined by the layer-doubling LEED analysis, i.e., $-\ -\ +\ \cdots$, with the largest quantitative discrepancy of about 0.04 Å. Comparison is made with LEED and DFT studies on other high-index Cu surfaces. Based on this comparison, a general trend for multilayer relaxations of open metal surfaces is proposed.

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I. INTRODUCTION

High-index (or open, vicinal, stepped) transition metal surfaces are of practical interest in areas such as heterogeneous catalysis. They have received attention since the early days of surface science.[1,2] However, detailed structure analyses on high-index surfaces started rather late in contrast to those on low-index surfaces. The main reason for this is that the principal technique for surface crystallography, quantitative low energy electron diffraction (LEED) analysis, encounters methodological difficulty when treating the closely spaced atomic layers in most high-index surfaces.

For a quantitative LEED analysis, the most efficient and extensively used the *k*-space method for calculating the intensity versus voltage (*I-V*) curves is the renormalized forward scattering (RFS) method.[3] However, the RFS method does not converge well for interlayer spacings less than about 1 Å.[4] Currently, the most practical solution for circumventing this difficulty is either to group several atomic layers throughout the surface into medium-sized slabs[5] or to simulate the whole surface region by a thick slab.[6] A common point in both solutions is that *l*-space methods are involved in the multiple scattering calculations within the slabs. The main difficulty of using *l*-space methods, e.g., the Beeby-type matrix-inversion method,[3] is the prohibitively long computing time which scales as the cube of the number of layers in the slabs. This scaling property makes *l*-space methods quite cumbersome for thick slabs. In this sense, another *k*-space method, the layer-doubling (LD) method,[3] may help. The LD method delays the divergence against the interlayer spacing due to the exact treatment of the multiple scatterings between two layers as opposed to the perturbative treatment in the RFS method. Interest in the LD method has been recently renewed. The tensor LEED scheme[7] has been implemented in this method by Materer.[8] However, few high-index surfaces have been successfully studied by the LD method. In this paper, we investigate the Cu(210) surface using the LD method. This surface has an interlayer spacing of 0.808 Å which is, to our knowledge, the smallest studied by the LD method. Our results show that the LD method works well for this surface.

Based on the quantitative LEED result of multilayer relaxation on Cu(210), this paper also investigates the accuracy of first-principles calculations on the structure of this surface. Clean high-index metal surfaces are suitable benchmarks for checking the current theoretical framework, since reliable experimental data on these surfaces are available. The results of multilayer relaxations on several high-index Cu surfaces from both quantitative LEED analysis and first-principles calculations have been reported. They include Cu(311),[9,10] Cu(331),[11,12] Cu(211),[12–14] Cu(511),[9,15] and Cu(711) (Refs. 6 and 9) surfaces. In terms of the interlayer spacing, Cu(210) lies between Cu(331) and Cu(211). The first-principles result on this surface, however, is still absent. We report, for the first time to our knowledge a first-principles pseudopotential calculation on Cu(210). By comparison with studies on other high-index Cu surfaces, a general trend for multilayer relaxations of open metal surfaces is proposed.

II. METHOD

A. Layer-doubling LEED analysis

The multilayer relaxations on Cu(210) have been investigated by two previous quantitative LEED studies.[16,17] The experimental *I-V* dataset used in this study is from Ref. 17. The dataset was collected at 130 K with a normal incidence of the electron beam as adjusted by a standard method.[17] The combined-space method[3] (CSM) was used in Ref. 17 for the multiple scattering analysis. Since the current study did not employ the tensor LEED approximation, we have cut the previous dataset into a shorter energy range, i.e., from 60 to 350 eV to facilitate the analysis. Finally, we used nine beams spanned in a $\Delta E = 2000$ eV energy range. Since only six structural parameters were optimized in this work, this dataset is believed to be sufficient.

The formalism for LD method setup by Van Hove and Tong[3] was used in this study. The program was written in

Fortran 90 language adopting the dynamic allocation of memory space which is important for implementing the energy-dependent features introduced later. The phase shift generation code is integrated into this program. Thus, no interpolation of the tabulated phase shifts is needed. The phase shift generation takes negligible computer cycles compared with the full-dynamical LEED (FD-LEED) intensity calculations. The basic linear algebra subroutines are called to do the multiplications and the inversions of the matrices involved in the LD formalism. The ion-core scattering phase shifts are generated by integrating the radial Schrödinger equation with the muffin-tin potentials as input. No relativistic effects were considered.

To improve the performance of the program, an energy-dependent number of beams (or plane waves) is employed. At each energy point, the number of beams (N_b) required for representing the wave field between two layers is estimated by[3] $N_b=(A/4\pi)[2E+(\ln t/d)^2]$, where A is the area of the surface unit cell, E is the incident energy corrected by the inner potential and d is the interlayer spacing. In this formula, energy is measured by Hartrees (27.2 eV) and length is measured by Bohrs (0.529 Å). t is a user-input dimensionless quantity which serves as the beam cutoff criterion.[3] In the current study we used 0.002 for t. This corresponds to about 90 beams at the low energy end (60 eV) and about 180 beams at the high energy end (350 eV). By using the energy-dependent N_b, the computing time for a FD calculation can be reduced by a factor of about 2. This scheme also results in a uniform error introduced by the beam cutoff throughout the whole energy range.

The number of ion-core scattering phase shifts was also made energy dependent, although the savings in computing time is marginal compared to the case in the matrix-inversion method.[18] Only phase shifts with absolute values larger than 0.001 were used in this study. This corresponds to seven phase shifts at the low energy end and 13 at the high energy end. The muffin-tin potential for Cu tabulated by Morruzi, Janak, and Williams[19] was used to generate the phase shifts.

The inner potential was taken to be energy independent in this study. The imaginary part (V_{0i}) was fixed at -4.5 eV, while the real part (V_{0r}) was optimized during the course of the best-fit structure search. The energy dependency of the inner potential for Cu has been studied by Rundgren[20] and successfully used in the study of the multilayer relaxation of Cu(711).[6] It has been shown that the systematic error introduced by nonconsideration of the energy dependency of V_{0r} is rather low (0.01 Å) and negligible by today's standards of quantitative LEED analysis.[21] Rundgren's energy-dependent V_{0i} for Cu was also tested in this study. It was found that the uncertainty due to the nonconsideration of the energy-dependency of V_{0i} was also less than 0.01 Å.

The temperature effect was taken into account by considering the isotropic thermal vibrations of the ion cores, which were incorporated in the temperature-dependent phase shifts. A Debye temperature of 343 K for Cu was used in this study, which corresponds to a vibration amplitude ($\langle u\rangle_{\mathrm{bulk}}$) of 0.086 Å for the bulk atoms at 130 K. The vibration amplitudes of the atoms in the topmost three layers ($\langle u\rangle_1$, $\langle u\rangle_2$, and $\langle u\rangle_3$) were enhanced by factors that were optimized in the best-fit search.

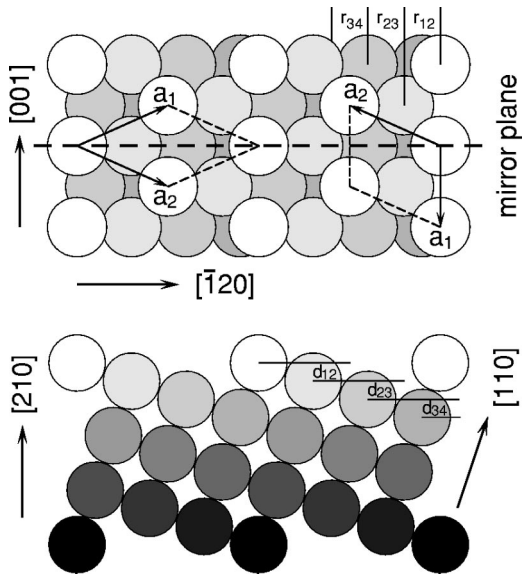

FIG. 1. Top view of Cu(210) surface and side view at the mirror plane. Four layers are visible from the top view. The registry repeats at every 11th layer as seen from the side view. The interlayer registries (r_{ij}) and the interlayer spacings (d_{ij}) of the topmost three layers are illustrated in the top and side views, respectively. Two equivalent surface unit cells are shown in the top view. The left one is used in the slab DFT calculations, the right one in the LEED analysis.

The Pendry R factor[22] (R_p) was adopted in this study to ascertain the agreement between the experimental and the theoretical I-V curves. Both the interlayer spacings (d_{ij}) and the interlayer registries (r_{ij}) of the topmost three layers as shown in Fig. 1 were optimized. The minimum R_p was located by a conventional grid search with a spacing of 0.01 Å.

B. Pseudopotential DFT calculations

Self-consistent periodic slab calculations within the framework of density functional theory (DFT) (Refs. 23 and 24) were conducted by the Vienna *ab initio* simulation package (VASP) (Refs. 25–27) to find the equilibrium ionic configuration of the Cu(210) surface. Starting from the bulk-truncated structure, VASP iteratively solves the Kohn-Sham equation for the electronic ground state of the current ionic configuration by using a plane wave basis set. After this calculation the ions are moved according to Hellmann-Feynman forces to predict a new trial ionic configuration. This process is repeated until the forces become less than 10 meV/Å. Only the plane waves with kinetic energies below 400 eV were included in our basis set.

The interactions between the ion cores and valence electrons are described by the Vanderbilt-type[28] ultrasoft pseudopotential (USPP) as supplied by Kresse and Hafner.[29] The generalized gradient approximation (GGA) of Perdew and Wang[30] was used for the exchange-correlation (xc) functional. To investigate the effects of different ion-core repre-

sentations and different xc approximations on the prediction of multilayer relaxations by first-principles calculations, the projector augmented wave (PAW) method[31] was compared with the USPP and the local density approximation (LDA) of Perdew and Zunger[32] was compared with the GGA.

The smearing method of Methfessel and Paxton[33] was used in this study to reduce the number of k points for total energy convergence. A smearing width (σ) of 0.2 eV was used for Cu. The zero temperature total energies were obtained by extrapolating to $\sigma=0$ eV.[27]

We first conducted calculations on bulk Cu using USPP-GGA, PAW-GGA, and USPP-LDA. The lattice constants (a_0) for fcc Cu obtained are 3.64, 3.64, and 3.53 Å, respectively. (Experimental $a_0=3.61$ Å.) These values were used in our slab calculations accordingly. In the bulk calculations, a grid of $10\times10\times10$ Monkhorst-Pack[34] k points was used for the Brillouin zone integration. This grid, in conjunction with the cutoff energy of 400 eV, is sufficient to converge the total energy per atom to about 1 meV as compared with a high precision calculation using $16\times16\times16$ k points and a cutoff energy of 500 eV.

The supercell approximation was employed in the current study, where the surface was simulated by slabs of atoms periodically arranged along the direction perpendicular to the surface. A 10-Å-thick vacuum layer was used to separate adjacent slabs in order to minimize the interactions between them. We used slabs consisting of 21 layers for the Cu(210) surface. For testing purpose, a 19-layer slab was also used.

For the slab calculations, a $6\times6\times1$ grid, which corresponds to 12 irreducible k points, was used, so that the product of the number of k points along a certain reciprocal basis vector and the length of the corresponding real basis vector approximately equals that in the bulk calculations (about 25 Å). The surface unit cell used in the slab calculations is rhombic as illustrated in Fig. 1.

III. RESULTS AND DISCUSSION

A. Layer-doubling LEED analysis

The parameters which give the best fit to the experimental I-V curves are listed in Table I. Also listed are the corresponding parameters from Ref. 17. Δd_{ij} and Δr_{ij} are the relaxations of d_{ij} and r_{ij}, respectively. They are defined as $\Delta d_{ij}=(d_{ij}-d_0)/d_0$ and $\Delta r_{ij}=(r_{ij}-r_0)/r_0$. d_0 and r_0 are the corresponding bulk values of d_{ij} and r_{ij}. It can be seen that the current LD FD-LEED analysis and the previous CSM tensor-LEED analysis give very similar results.

The best-fit calculated I-V curves are compared with the experimental ones in Fig. 2. The average R_p between the two sets of curves is 0.12 and the variance of R_p, var(R_p), is 0.016 as evaluated by Pendry's formula,[22] $\mathrm{var}(R_p)=R_p\sqrt{8|V_{0i}|/\Delta E}$. This result is comparable to the best achieved on high-index surfaces, i.e., on the Cu(711) surface where $R_p=0.12$ and $\mathrm{var}(R_p)=0.013$ were reported.[6] A direct inspection of Fig. 2 also confirms the excellent agreement between the two sets of I-V curves. *All* detailed features exhibited in the experimental curves have been reproduced by our calculations except for several regions where a small peak becomes a shoulder, or vice versa. This agreement was not achieved in the previous studies.[16,17]

TABLE I. Optimized structural and nonstructural parameters which give the best fit to the experimental I-V curves.

	This work	Ref. 17
Δd_{12} (%)	-11.1 ± 1.9	-11.1 ± 2.0
Δd_{23} (%)	-5.0 ± 1.6	-5.7 ± 2.3
Δd_{34} (%)	$+3.7\pm1.7$	$+3.8\pm2.5$
d_0 (Å)	0.808	0.808
Δr_{12} (%)	-1.9 ± 2.9	-1.8 ± 3.0
Δr_{23} (%)	-1.9 ± 2.5	-2.5 ± 3.2
Δr_{34} (%)	$+0.6\pm2.6$	$+1.7\pm3.5$
r_0 (Å)	1.616	1.616
$\langle u\rangle_1$ (Å)	0.138	0.134
$\langle u\rangle_2$ (Å)	0.112	0.096
$\langle u\rangle_3$ (Å)	0.103	-
$\langle u\rangle_{\mathrm{bulk}}$ (Å)	0.086	0.086
V_{0r} (eV)	-6.0	-5.99
V_{0i} (eV)	-4.5	-4.0 [a]
R_p	0.12	0.15
$var(R_p)$	0.016	0.017 [b]

[a]Energy dependent.
[b]Estimated by taking $V_{0i}=-4.0$ eV.

Dynamical (multiple scattering) features, such as weak peaks and shoulders, in I-V curves are crucial for quantitative LEED analysis. In the current study the accurate reproduction of both the kinematic (single scattering) and the dynamical features in the experimental I-V curves implies that the LD method works well for high-index metal surfaces with the interlayer spacings down to at least 0.8 Å, in particular, for materials in which the multiple scattering is not very strong.

When conducting structural studies on chemisorption systems, sufficient models have to be considered. A quantitative LEED analysis on these systems using the l-space methods is usually tedious even with the tensor-LEED scheme.[35] This work should pave the way for future studies on various chemisorption systems on Cu(210) surface and other similar surfaces, such as Ni(210).

B. Pseudopotential DFT calculations

The multilayer relaxations of the Cu(210) surface by pseudopotential DFT calculations using four different setups are listed in Table II. For the USPP-GGA calculation with a 21-layer slab, it can be seen that only the topmost three layers relax significantly and the relaxation sequence is consistent with the LEED analyses, i.e., $-\ -\ +\ \cdots$, where "$-$" denotes a contraction, "$+$" an expansion, and "$\cdots$" means that the sequence followed is not definite due to the small relaxations. However, quantitative differences from the relaxations in Table I are observed.

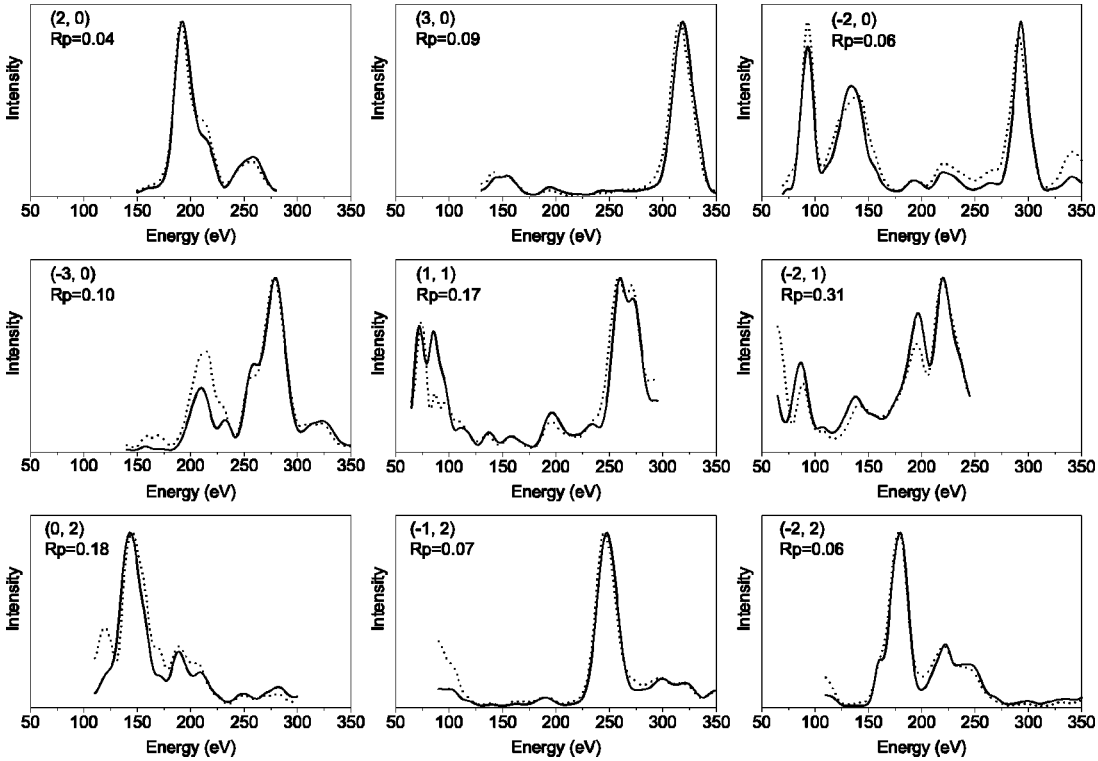

FIG. 2. Comparison of experimental (solid line) and best-fit theoretical (dotted line) I-V curves for the Cu(210) surface. The experimental curves were measured at $T=130$ K (Ref. 17).

Comparing the second and third columns in Table II, it can be seen that the largest difference between the results calculated from a 19-layer slab and a 21-layer slab is 1.7% for Δd's and 0.5% for Δr's. This implies that the error introduced by a finite thickness slab is about 0.015 Å. In view of other approximations employed in our calculations, such as the non-zero residual forces, the k-point sampling and the plane wave cutoff, we estimate that the total errors in the final ionic positions are about 0.02 Å.

TABLE II. Multilayer relaxations of Cu(210) surface from pseudopotential DFT calculations.

	USPP GGA 21-layer	USPP GGA 19-layer	PAW GGA 21-layer	USPP LDA 21-layer
a_0 (Å)	3.64	3.64	3.64	3.53
Δd_{12} (%)	−16.4	−16.5	−17.1	−17.0
Δd_{23} (%)	−4.5	−6.2	−4.8	−4.2
Δd_{34} (%)	+7.2	+7.4	+7.0	+6.6
Δd_{45} (%)	−0.6	−0.5	−1.2	−1.3
Δd_{56} (%)	−0.9	−1.3	−0.9	−0.8
Δd_{67} (%)	+1.4	+0.7	+0.8	+0.9
Δr_{12} (%)	−1.1	−1.2	−1.0	−0.9
Δr_{23} (%)	−1.0	−1.2	−0.8	−1.0
Δr_{34} (%)	+2.0	+2.4	+2.4	+2.0
Δr_{45} (%)	−1.0	−0.5	−0.8	−0.9
Δr_{56} (%)	−1.2	−1.0	−1.2	−1.3
Δr_{67} (%)	−0.3	−0.1	−0.4	−0.4

As can be seen from Table I, LEED is less sensitive to Δr as compared to Δd. In our study the error bars for the Δr's are always larger than 0.04 Å, while always smaller than 0.02 Å for the Δd's. In view of this, we can say that the discrepancies in Δr's are acceptable. Considering the aforementioned errors in our DFT calculations as well as the accuracy of LEED in the determination of Δd, we think that only discrepancies in Δd smaller than 0.04 Å are acceptable excluding the temperature effect discussed later. Judged by this criterion, only the discrepancy in Δd_{12} (about 0.043 Å) is slightly large.

The result using the PAW method is listed in the fourth column of Table II. It can be seen that the PAW does not improve the discrepancy. Table II also shows that the LDA gives similar results to the GGA even though the difference between the bulk lattice constants is larger than 0.1 Å.

Another possible reason that may account for the discrepancies is the temperature-dependency of relaxations, which is recently attracting more attention. Both thermal expansion and contraction of relaxations have been observed on open metal surfaces.[36–38] However, due to the limited number of temperature-dependent studies on multilayer relaxations of high-index surfaces, the picture of the dependency is not clear yet. Nevertheless, due to the low temperature (130 K)

TABLE III. Comparison of multilayer relaxations of high-index Cu surfaces from quantitative LEED analysis and slab DFT calculations.

	Cu(311)		Cu(331)	
	LEED Ref. 10	USPP Ref. 9	LEED Ref. 11	FLAPW Ref. 12
Δd_{12} (%)	−11.9	−15.0	−13.8	−22.0
Δd_{23} (%)	+1.8	+4.0	+0.4	+1.6
Δd_{34} (%)			+4.0	+6.9
Δd_{45} (%)			−4.0	−2.4
	Cu(210)		Cu(211)		
	LEED This work	USPP This work	LEED Ref. 14	FLAPW Ref. 12	PP Ref. 13
Δd_{12} (%)	−11.1	−16.4	−14.9	−28.4	−14.4
Δd_{23} (%)	−5.0	−4.5	−10.8	−3.0	−10.7
Δd_{34} (%)	+3.7	+7.2	+8.1	+15.3	+10.9
	Cu(511)		Cu(711)	
	LEED Ref. 15	USPP Ref. 9	LEED Ref. 6	USPP Ref. 9
Δd_{12} (%)	−14.2	−11.1	−13.0	−9.3
Δd_{23} (%)	−5.2	−16.4	−2.0	−7.7
Δd_{34} (%)	+5.2	+8.4	−10.0	−21.8
Δd_{45} (%)	−1.2	−4.6	+7.0	+14.3
Δd_{56} (%)	+3.2	+2.3	−1.0	−3.0
Δd_{67} (%)	−3.1	−1.5	−4.0	−9.1
Δd_{78} (%)	−3.3	+0.2	+7.0	+5.6

at which the LEED dataset for Cu(210) is collected, the temperature effect should not be very significant.

C. Comparison with other high-index Cu surfaces and general trend of multilayer relaxations

In Table III we compare the multilayer relaxations of high-index Cu surfaces by a quantitative LEED analysis and slab DFT calculations. We see that all slab DFT calculations reproduce the relaxation sequences obtained by LEED analyses. However, the extent of quantitative agreement between LEED and DFT differs from one study to another. For instance, the pseudopotential (PP) study in Ref. 13 shows an excellent agreement with the LEED study,[14] while the full-potential linearized augmented plane wave (FLAPW) study[12] on the same surface gives rather large discrepancies.

In Table III we notice that (210) has the same relaxation sequence as (211) and (511). Inspired by this hint, we propose a general trend for the multilayer relaxations of open metal surfaces. At bulk-truncated configuration, define a *surface slab* in which the nearest neighbors (nn's) of all atoms are fewer than those in the bulk. In the process of relaxation, the interlayer spacing between each pair of layers within this slab contracts, while the spacing between this slab and the substrate expands.

TABLE IV. Relation between nn sequence and relaxation sequence of high-index surfaces of fcc structure. N is the number of layers in the *surface slab* (see the text).

Orientation	nn sequence	N	Relaxation sequence
(311)	(7,10,12···)	2	$-+\cdots$
(331)	(7,9,11,12···)	3	$--+\cdots$
(210)	(6,9,11,12···)	3	$--+\cdots$
(211)	(7,9,10,12···)	3	$--+\cdots$
(511)	(7,8,10,12···)	3	$--+\cdots$
(711)	(7,8,8,10,12···)	4	$---+\cdots$

In this rule, we relate the relaxation sequence of a surface to the changes in the number of nn's. The nn sequences for the six fcc surfaces in Table III are given in Table IV. Taking (210) as an example, the nn sequence(6,9,11,12, . . .) means that, in a bulk-truncated configuration, the atoms in the first layer have six nn's, the second layer nine and the third 11. From the fourth layer downwards, the number recovers to 12, the value in the bulk. Thus, according to the trend above, the *surface slab* of fcc (210) consists of three layers and the interlayer spacings within this slab (i.e., d_{12} and d_{23}) contract, while the spacing between this slab and the substrate (i.e., d_{34}) expands. Hence, the relaxation sequence is $--+\cdots$. The rest of Table IV can be deduced by analogy. We want to mention that, except for the fcc high-index surfaces listed in Table IV,[42] our proposed rule is also applicable to open surfaces of bcc and hcp structures. A violation of this rule in Table III is Cu(331), where a relaxation sequence of $-++\cdots$ was deduced from a LEED study[11] and was reproduced by a FLAPW study.[12] Systematic evaluation of this rule, as well as detailed discussion on Cu(331), will be published separately.[43]

The relaxation rule presented above is consistent with Smoluchowski's concept of charge smoothing,[39] which has been adopted to explain the multilayer relaxations for a long time.[12,40,41] According to this concept, at metal surfaces, the nearly free electrons tend to spread towards regions of low charge density and smooth the corrugation formed by the ion cores. In this process, the ion cores in deeper layers shift towards the surface, induced by the movement of the electrons, and result in contraction of the interlayer spacings near the surface. The more open the surface, the more the electrons from the deeper layers contribute to the smoothing; hence the more spacings contract. The expansion involved in the relaxation sequence may result from the residual dipole in the *surface slab* due to the incoherent movements between the electrons and the ion cores.

IV. CONCLUSION

We have studied the multilayer relaxation of the Cu(210) surface using layer-doubling LEED analysis and pseudopotential DFT calculations. The best-fit calculated I-V curves show an excellent agreement with the experimental ones as judged by both visual inspection and a small R_p (0.12). This

implies that the LD method is a suitable choice for quantitative LEED analyses on high-index metal surfaces with interlayer spacings down to 0.8 Å. Based on this reliable LEED result, we investigated the accuracy of the DFT calculations on the prediction of the structure of Cu(210). Our pseudopotential DFT calculations give the correct relaxation sequence of this surface, i.e., $-\ -\ +\ \cdots$, with the largest quantitative discrepancy of about 0.04 Å. A general trend for the multilayer relaxations of open metal surfaces has also been proposed.

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[42] This relaxation rule has been checked on high-index Cu surfaces with interlayer spacings down to 0.44 Å by pseudopotential DFT calculations. No violation has been found.
[43] We have performed a systematic study on the (331) surfaces of seven fcc metals, including Ni, Cu, Rh, Pd, Ag, Ir, and Pt, by pseudopotential DFT calculations. This study shows that all these surfaces have a relaxation sequence of $-\ -\ +\ \cdots$. No anomalous behavior was found on Cu(331).